Molecules from Space and the Origin of Life

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There is a growing concensus among space scientists that frozen molecules from space helped to make the Earth the pleasant place that it is today, and helped Life start on Earth, and perhaps elsewhere. The chain of logic that led scientists to posit a connection between extraterrestrial molecules and the origin of life is as follows. 1) The rapidity with which life arose demands that conditions on Earth were conducive to the formation of life very early on. 2) There is reason to believe that comets and meteorites fell on the Earth from its inception. 3) We now know that comets and meteorites are replete with complex organic compounds, some of which resemble those in living systems. 4) Perhaps the input of molecules from comets and meteorites provided crucial constituents to the primordial soup and jump started life on Earth. 5) These molecules formed out in deep space long before the Earth ever existed, by processes that we can reproduce in the laboratory. 6) The fact that organic molecules are seen by astronomers throughout our galaxy and in others makes it seem likely that they were (and are) available to help start life in other planetary systems.

The oldest microfossils demonstrate that life was certainly established on the Earth 3.5 billion years ago, and there is isotopic evidence that suggests life as early as 3.8 billion years ago, and possibly earlier.

Although the Earth is roughly 4.55 billion years old, this is very early for life to have arisen since there is reason to believe that the Earth was

sterilized regularly by collisions with large bodies until about 4 billion years ago. In other words, only a couple of hundred million years after the earliest point that Earth possibly could have safely supported life, (quite fast in geological terms) there were already organisms established well enough that evidence of it remains today. This is quite remarkable and implies that terrestrial life must have arisen very rapidly. Perhaps life even arose and was extinguished multiple times by blows from extraterrestrial bodies before it finally took hold.

Presumably life was preceded by complex biotic molecules (like those that make up living systems), but where they came from is unclear. The now famous Miller-Urey experiments in the early 1950s showed that such biotic molecules could be produced in a simulation of the young Earth that consisted of simple molecules, liquid water, and a spark discharge. It was believed that the water, air and all the other chemical ingredients that went into the primordial soup were already in the Earth from the time of its formation. Since then, this notion has been challenged by new knowledge and theories.

Some scienctists suspect that the forming Earth was so hot that much of the original water and air would have escaped. Furthermore, at that time, Earth was hit more often by large chunks of debris left over from the formation of the Solar System, causing cataclysms equivalent to the detonation of countless atom bombs. For example, the Moon is thought to

have been created in such an event when a Mars-sized object collided with the Earth. Surely such impacts aborted any nascent life on the Earth at that time, and perhaps deprived the Earth of some of the air and water it had retained. [Fig. 1, a big impact]

It has been periodically proposed (most recently by Dr. Chris Chyba of the SETI Institute) that some of our water and gases came from the outside to the Earth. The most likely conveyor of molecules would be small comets, meteorites and interplanetary dust particles (IDPs), tiny grains of comet and asteroid dust that litter the inner solar system and are swept up by the Earth all the time. The largest ones are perhaps as big as a grain of sand and can sometimes be seen in the night sky as shooting stars. It has been estimated that roughly 10 tons of IDPs drift down to the Earth's surface each day. [Figure 2, an IDP under the microscope and a NASA ER2 (U2) plane used for collection]

We do not know if the Earth really lost all, or even most, of its air and water early in its existance, However, it is clear that the Earth has received large quantities of meteorties and dust particles so there must have been some input from extraterrestrial materials early in the Earth's existance. The extraterrestrial delivery of even simple molecules from space has some obvious implications.

First of all, if the Earth received enough water from comets to make even part of our oceans, then other planets must have too. While water

was raining down throughout the inner solar system, the conditions on the other planets were not favorable for forming and mantaining life. Some were too small, some were too hot, only the Earth was just the right size, and in just the right place, to retain its water and air so it could harbor life for billions of years. Second, there is now strong evidence that in addition to gases and water biotic molecules, of the sort seen in the Miller-Urey experiments, were brought to us ready made by extraterrestrial objects such as meteorites and IDPs.

Most meteorites are composed of metal and rock, [Fig. 3 a meteorite pic] but some are well known to contain complex organic molecules including ketones, carboxylic acids, amines, amides, an ensemble of sulfur compounds, and many more. A lot of the carbon in these meteorites is tied up in kerogen, a messy coal-like substance, and a wide distribution hydrocarbons including polycyclic aromatic hydrocarbons (PAHs), the class of compound that attracted attention when they were detected in ALH 84001, the controversial Martian meteorite that displayed characteristics consistent with fossilized Martian microbes.

The most interesting meteoritic molecules are of the same chemical class as those in living things, and posses properties that may relate to our biology. For example, around fifty extraterrestrial amino acids (the building blocks of proteins) have been extracted from meteorites, and recent reports, by Professor. John Cronin of Arizona State University,

demonstrate a slight surplus of left handed molecules in certain cases.

Since most amino acids in living things are left handed, this provocative result suggests that our own molecular left-handedness may have been predetermined by that of extraterrrestrial amino acids!

Furthermore, Dave Deamer of U. C. Santa Cruz has shown that when organic compounds from Murchison are mixed with water they spontaneously assemble into membrane-like structures. Perhaps the tendency of these molecules to aggregate in this manner may have been instrumental in the formation of the first membranes, a trait that may have been taken advantage of by the earliest organisms.

We have proof that comets, too, are a source of organic compounds. Pictures of Comet Halley showed dark material on the surface that looked like the tar produced in the Miller-Urey experiment. Spectroscopic analysis (what frequencies of light, both visible and not, are absorbed) of comets and comet-like bodies in the outer solar system indicate the presence of organic molecules on their surface. Instruments on board Giotto and the Vega space craft measured fragments of molecules as they zipped past Halley at around 250,000 Km per hour. And most recently, a number of specific organic compounds including CH₄, CH₃OH, CH₃CH₃, NH₂CHO, HCOOH, and HCOOCH₃ were remotely detected in the gas around comets Hyakutake, and Hale-Bopp.

These comet molecules are not only out there, they also come to us. Dust is released by comets in profusion when they pass through the inner solar system and some is swept up by the Earth. Some of this comet dust, in the form of IDPs, are collected by NASA in the upper atmosphere using U2 aircraft (Fig. 2) and brought to scientists for testing. These microscopic particles can be as much as 50% organic carbon, more than any other known extraterrestrial object., and IDPs alone add at least a ton of organic material to the biosphere every day.

IDPs and meteorites contain some very large organic compounds, some comprised of hundreds of carbons atoms. For example, carbon-rich compounds weighing hundreds of atomic mass units (amu) have been detected in IDPs, and as high as 5000 amu were recently measured by Luann Becker et al. in meteorites. To put this in context one carbon atom weighs 12 amu, vitamin C is 176, prostaglandins and steroids are 400-500, neurotrasmitters are in the range of 1000, and most proteins are many thousands of amu.

So, not only did comets, IDPs and meteorites bring water to the Earth they also brought complex organic molecules, some of which are as big as those seen in living systems. Perhaps these compounds played a role in the development of life on this planet. If our solar system is unusual in having this supply of organic materials then we were very lucky and life would, indeed, be very rare. But if such molecules are wide spread across

many planetary systems then we know that at least one essential prerequisite for life is commonly available.

There are basically two different notions about where these extraterrestrial organic molecules came from. Some say that the water and other molecules that make up comets have gone through the solar nebula, the hot swirling disk of dust and gas from which the sun and planets formed. According to this model the ice sublimed and probably the molecules were even broken and reformed in the process that made the planets. (Sublimation is the process by the way in which ice cubes left for a long time in a self-defrosting fridge, will slowly diminish). Others contend that the molecules originated in the gigantic dark clouds of dust and ice out in the interstellar medium, the kinds of clouds from which our own solar system formed. [Fig. 4, see below]

The latter (interstellar) model was bolstered recently by the striking similarity between specific molecules detected lately in comets and those commonly measured by astronomers in insterstellar ice grains. For example, the amount of methanol, relative to water, in many comets is close to that found in the insterstellar medium. Furthermore, the quantities and relative proportions of methane to ethane and HCN to HNC in Hyakutake seem consistent with an interstellar origin. In addition, the ortho to para ratio (a measure of the conditions the ice has experienced) of

the water from Hale-Bopp establishes that the ice formed at, and was never warmed above, $\sim\!25$ K (-400° F; -250° C).

This strongly suggests that the ice grains that comprise Hale-Bopp formed in the interstellar medium and aggregated into a comet well below temperatures that would normally sublime ice and break bonds. On the other hand, there is evidence that liquid water percolated through the Murchison meteorite presumably at a time when it was part of a larger body, like a comet. Perhaps comets that were never heated on the outside melted near the center as a result of the decay of radionuclides at the core, the source of the Earth's internal heat.

The truth about the origin of cometary and meteoritic molecules is almost certainly in-between the pure interstellar ice box and the nebular fire storm. This is manifest in many chondritic meteorites which contain components that have been modified by great heat, right next to others that have not. In other words, materials that were fried in the solar nebula got mixed in with more pristine matter, but there is no avoiding the fact many of these cometary and meteoritic molecules must have formed in the space between the stars before the sun and solar system existed.

How do these complicated molecules form in the space between the stars where the temperature is so low that N_2 and O_2 (the major components of air) are frozen solid? Thanks to great strides in observational capabilities coupled with lab experiments dedicated to

reproducing conditions germane to astrophysics, scientists have learned a tremendous amount about what molecules are present in space.

By comparing the spectrum seen at the telescope to measurements made in the lab, scientists have determined that the dark clouds, like the horsehead nebula seen in figure 4, are comprised of tiny sand-like grains each covered by a thin layer of ice. The average temperature in these clouds is about 20 K (about -420° F; -250° C) and the whole dust grain is perhaps one ten thousanth of a millimeter across. The ice is composed primarily of water but often contains some (1-10%) simple molecues like carbon dioxide, carbon monoxide, methane, methanol, and ammonia. It is amazing that we can determine the molecular composition of microscopic particles of dust and ice hundreds of light years away.

To understand how these very simple, abundant, molecules undergo reactions to produce the more complicated compounds, like those seen in meteorites, we conduct sophisticated laboratory simulations (Fig. 5). We expose those simple molecules seen by astronomers to conditions, in the lab, equivalent to what they experience in the interstellar medium. The lab experiments show that even at the extremely low temperatures and pressures of space the omnipresent radiation breaks bonds and makes simple compounds become more complicated. This means that out in space, everywhere these ice grains are seen, complex organic compounds

are being formed. Our lab experiments allow us to determine what these molecules are without having to go out there and get them.

For example, we have shown that a simple mixture of water, methanol and ammonia, all of which are seen as ice in space, will break and recombine under the influence of ultraviolet (UV) radiation to yield ethanol CH₃CH₂OH, formamide {HC(=O)NH₂}, acetamide, {CH₃C(=O)NH₂}, ethers, and alcohols, related to the polymer of formaldehyde {POM, (-CH₂O-)_n}, and hexamethylenetetramine (HMT, C₆H₁₂N₄), which weighs in at 140 amu. Compounds of greater biological significance have been made from simulations that begin from more complex interstellar organic compounds such as PAHs.

PAHs are flat molecules of carbon and hydrogen in the form of hexagons so that their skeleton looks like chicken wire. They are common pollutants, often carcinogens, and found on Earth in coal, soot, broiled hamburgers, and automobile exhaust. Dr. Allamandola (one of the authors) has previously shown that PAHs are the most abundant class of carbon-containing compounds in the Universe, and are expected to freeze out into the ice mantles in dark clouds.

Earlier this year we reported on our study of the photochemistry of PAHs in water ice in the journal Science (editor: this is scheduled to appear in the Feb 19th issue). When these experiments are performed in ice made

from deuterated (heavy) water the deuterium is incorporated onto the PAHs. This may explain why the PAHs seen in meteorites carry so much deuterium. We showed that under interstellar conditions the PAHs are converted to alcohols, ethers and perhaps most importantly quinones, all of which have been detected in meteorites.

Quinones are ubiquitous in living systems today appearing commonly in medications and cosmetics. For example, the acitve ingredients in aloe, St. John's Wort and Henna are all quinones (Figure 6). Because of their ability to stabilize unpaired electrons, quinones are involved in electron transport, an essential celluar process. Furthermore, PAHs strongly absorb UV radiation so they may have acted as UV shields on the early earth, back before there was an ozone layer. Such compounds, that combine the capacity to absorb radiation and act in electron transport, may have been the first molecules that our ancestors used to harness light energy.

Most recently, Dr. Jason Dworkin, of our lab at NASA Ames, has made molecules, weighing 100-1000 amu, that are very similar to those seen in meteorites and IDPs, and many also posses properties that make them biologically important. For example, complex mixtures produced in his recent (unpublished) lab simulations come together to make membrane-like structures that resemble those made by extracts from the Murchison meteorite (see above).

So, we know from laboratory experiments that in the seemingly barren and harsh conditions of deep space complex compounds form as a result of the ambient radiation field. Meteorites, and IDPs bring these interstellar molecules to us even today. Since objects like Asteroids, comets, and their dust should get swept up as time goes on, it also means that the Earth probably got hit a lot more often, and picked up alot more molecules, earlier in its existence.

If we now reconsider the development of life with this in mind we can see that the arrival of amino acids, quinones, and other molecules that make membranes, may well have made it possible for life to develop, or at least facilitated the process. One can imagine that a molecule, that literally dropped from the sky, could have allowed or accelerated a simple chemical reaction for some early organism(s) able to exploit it. Being able to carry out this chemistry more efficiently could confer an evolutionary advantage, if the ability were passed on to progeny. In time, that simple reaction would become deelply embedded in what is now a biochemical process that is regulated by a protein that has been optimized by billions of years of selective pressures.

Of course there is still a huge gap between molecules, no matter how complex, and life. But these organic molecules are seen everywhere, even in other galaxies, so if they had something to do with life here that means that they were, and are, also available to help with the development of life

elsewhere. The ubiquity of these molecules across space, combined with the recent discoveries of about 16 planets around other stars, makes it seem more likely that at least the conditions conducive to life, if not life itself, have developed in other solar systems.

Figures:

- Figure 1. Earth shattering collision.
- Figure 2. IDP microscope image and NASA U2 plane photo.
- Figure 3. A meteorite, perhaps with Scott in the Antarctic.
- Figure 4. light (a line) from a star (from a hubble photo of say the horsehead nebula) comes down to a drawing of an observatory on the surface of earth and a comet flies overhead. Inset 1 from the cloud shows an ice grain with molecules on the mantle. Inset 2 from along the path of the lines of light from the comet and cloud shows three different labelled curves that look alike, one from the nebula (similar pinkish color), another from the comet (white) and the last from the lab, another color.
- Figure 5. Photos of lab equipment. Perhaps we can superimpose a scheme showing some chemical reactions observed in the ice on a close up of the IR window bathed in the pink glow of the UV lamp.
- Figure 6. Chemical equations showing some quinones in nature and the correspoding PAHs. i.e. Juglone (in walnut and aloe), St. Johns Wort, etc

Dr. Max Bernstein is at NASA Ames through a cooperative agreement with the SETI Institute, in Mountain View, CA. He works in the lab simulating the organic chemistry of comets and interstellar ice grains, and its connection to the origins of life. Drs. Scott Sandford and Louis Allamandola are both civil servants at NASA's Ames Research Center. Dr. Sandford performed seminal work on IDPs, is an editor of the journal Meteoritics and Planetary Science, and has found many meteorites in Antarctica, including a piece of the Moon. Dr. Allamandola has 20 years

years of experience in pioneering laboratory studies of interstellar and solar system ices and is an originator of the PAH hypothesis. All three work at the Astrochemistry Lab, and you can read more about them, their scientific research, and the other people who work there by visiting the web page at: http://www-space.arc.nasa.gov/~astrochem/

Suggested reading:

"Forging New Planets: The Origin of Our Solar System" J. A. Wood Sky and Telescope, Jan 1999, vol 97, #1 p 36.

"Moon-Froming Crash is Likely in New model," D. Mackenzie, Science, vol 283, 1 Jan, 1999. pp. 15-16

"Deconstructing The Moon" R. Jayawardhana, Astronomy Sept. 1998 vol 26, #9.

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"The Kuiper Belt" J. X. Luu, D. C. Jewitt Scientific American May 1996 vol 274, #5, p 46

"The Constraints of Chance" C. deDuve Scientific American Jan 1996, Vol 274, #1, p112.

"Life in the Universe" Special Issue of Scientific American Oct. 1994

"The Cosmic Origins of Life on Earth," C. Chyba, Astronomy November 1992, Vol 20, #11, pp. 28-35.

For students of the subject or advanced amateurs:

Comets and the Origin and Evolution of Life, eds. P.J. Thomas, C.F. Chyba, and C.P. McKay, Springer, New York, 1997.

"The Astrochemical Evolution of the Interstellar Medium" E.L.O. Bakes from Modern Astrophysics: A Graduate Series H. A. Thronson ed. Kluwer Academic Publishers. Netherlands 1997.

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